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PROCESSING ALTERNATIVES FOR DESTRUCTION OF TETRAPHENYLBORATE

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ABSTRACT

Two processes were chosen in the 1980's at the Savannah River Site (SRS) to decontaminate the soluble High Level Waste (HLW). The In Tank Precipitation (ITP) process (1,2) was developed at SRS for the removal of radioactive cesium and actinides from the soluble HLW. Sodium tetraphenylborate was added to the waste to precipitate cesium and monosodium titanate (MST) was added to adsorb actinides, primarily uranium and plutonium. Two products of this process were a low activity waste stream and a concentrated organic stream containing cesium tetraphenylborate and actinides adsorbed on monosodium titanate (MST). A copper catalyzed acid hydrolysis process was built to process (3, 4) the Tank 48H cesium tetraphenylborate waste in the SRS's Defense Waste Processing Facility (DWPF). Operation of the DWPF would have resulted in the production of benzene for incineration in SRS's Consolidated Incineration Facility. This process was abandoned together with the ITP process in 1998 due to high benzene in ITP caused by decomposition of excess sodium tetraphenylborate. Processing in ITP resulted in the production of approximately 1.0 million liters of HLW.

SRS has chosen a solvent extraction process combined with adsorption of the actinides to decontaminate the soluble HLW stream (5). However, the waste in Tank 48H is incompatible with existing waste processing facilities. As a result, a processing facility is needed to disposition the HLW in Tank 48H.

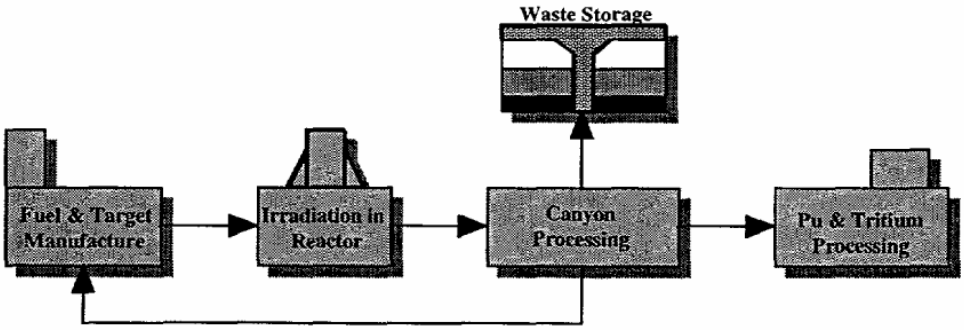
This paper will describe the process for searching for processing options by SRS task teams for the disposition of the waste in Tank 48H. In addition, attempts to develop a caustic hydrolysis process for in tank destruction of tetraphenylborate will be presented. Lastly, the development of both a caustic and acidic copper catalyzed peroxide oxidation process will be discussed.

INTRODUCTION

How the Waste Was Generated

Since the early 1950's, the Savannah River Site operated a nuclear fuel cycle to manufacture nuclear materials for the US defense program. Fuel and target elements were fabricated and irradiated in reactors to produce the desired materials (Fig. 1.). After removal from the reactors, the targets and fuel elements were chemically processed through the canyon facilities (F and H Canyons) - so-called because of their long, narrow enclosed structure designed for shielding and remote maintenance. Fuel was recovered and recycled for fabrication into new fuel elements and the desired products (plutonium and tritium) extracted for further processing. The extraction process involved dissolving the targets and fuel elements in nitric acid and produced a substantial waste stream. Since stainless steel was in critically short supply in the early 1950's, the waste was neutralized to a high pH with caustic before being stored in buried carbon steel tanks. During the 40 years of operation, about 320 million liters of high level radioactive waste were generated. -

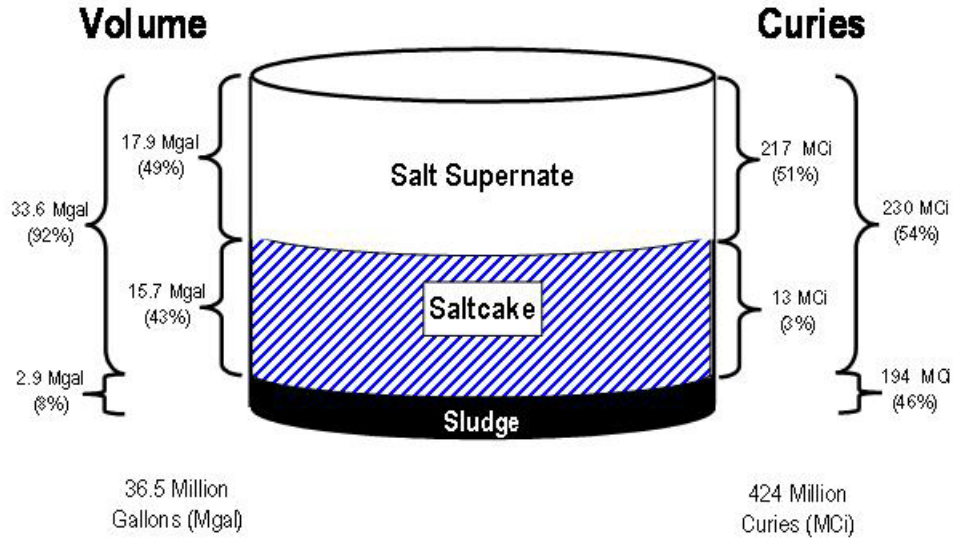
Fig. 1. Schematic of SRS processing that led to the creation of the HLW.



How the waste is stored

The waste is stored in alkaline form in 4.9 million liter carbon steel tanks (Fig. 2.). Most of the metal ions (primarily aluminum, iron, and transition metals) precipitate as oxides or hydroxides known as sludge, while alkali metals and anions (e.g., sodium aluminate, sodium nitrate) stay in solution as dissolved salts. Most of the radioactive elements are in the sludge, except for Cs^{137} which is found in the dissolved salt solution (supernate). The sludge is allowed to settle and the salt solution is decanted to another tank. To conserve storage space, the salt solution supernate is concentrated by evaporation beyond saturation. As the evaporator bottoms cool, the alkali salts precipitate to form "saltcake." The evaporator overheads flow to the Effluent Treatment Facility (ETF) where the waste water is filtered and treated to remove mercury, organics, salts, and any residual Cs, then released at a permitted outfall. Solids and salts removed in ETF are concentrated by evaporation and sent to Z Area. After evaporation, the Tank Farm waste is in three forms: sludge, saltcake and supernate. Through evaporation, the original waste volume of 85 million gallons (320 million liters) has been reduced to a total of about 34 million gallons (130 million liters).

Fig. 2. Schematic showing waste volume and curies of sludge, salt cake and supernate in SRS HLW tanks as of March 31, 2006. Approximately half of the radioactivity is from the sludge and half in the salt supernate.



ITP Description

The ITP process was developed in 1980 by Lee and Kilpatrick (6) as a less expensive option for removing cesium from the salt waste than the use of ion exchange resin. Cesium tetraphenylborate is extremely insoluble. The addition of sodium tetraphenylborate to SRS Soluble HLW reduces the radioactive Cs^{137} concentration by a factor of 40,000. This would have allowed the decontamination of the salt portion of the HLW (currently approximately 160 million liters). The decontaminated salt solution could then be inexpensively immobilized in grout at SRS, while the highly radioactive stream could be concentrated to minimize the processing volume. Fig. 3. is a schematic showing the major processing facilities involved in the ITP Facility.

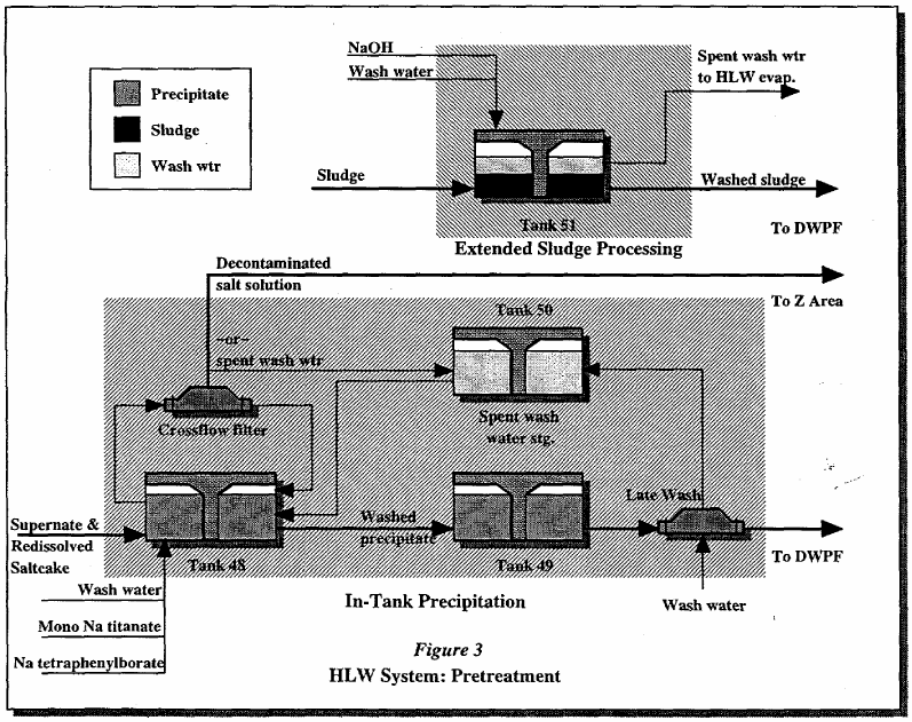


Figure 3
HLW System: Pretreatment

The ITP facility at the Savannah River Site began radioactive operation in September of 1995. During slurry pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected, although the lower flammability limit for benzene in air was never approached. In August 1996, the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1 that recommended additional operation and testing not continue in the ITP facility until the mechanisms of benzene generation, retention, and release were better understood.

On January 23, 1998, the Westinghouse Savannah River Company recommended to the DOE that facility modifications should be suspended on the In-Tank Precipitation facility, since results from chemical tests failed to resolve concerns about benzene generated by the process using the current plant configuration. The recommended suspension was accepted by the DOE.

Tank 48H Legacy

The 1.0 million liters of waste in Tank 48H is incompatible with existing waste processing facilities. As a result, a processing facility is needed to disposition this waste and return the tank

to service as the feed tank for the planned Salt Waste Processing Facility. Tetraphenylborate waste has been stored in Tank 48H since 1983 and is very chemically stable. Based on periodic sampling, the KTPB solids presently stored in Tank 48H are not chemically decomposing at a measurable rate. The observed rate of increase of potassium in solution is consistent with the expected rate of decomposition from radiolysis alone (< 1 mg/L-hr). Maintaining the temperature at less than 35 'C and the [OH^-] greater than 0.6 M will assure the long-term stability of stored KTPB. Presently, the slurry in Tank 48H contains [OH^-] in excess of 1 M and the temperature is less than 30 'C. The tank is sampled periodically to monitor the concentration of hydroxide. The safety of continued storage under these conditions is also supported by more than 10 years of safe storage of KTPB in Tank 48H following the 1983 demonstration (7,8) and more than 10 years of storage since the shutdown of the ITP process.

Development of Tank 48H Processing Alternatives

The first major effort to develop processing alternatives was initiated in FY2001 (9,10). A High Level Waste (HLW) Tank 48H Disposition Team was formed on in December 2001. The Team was chartered to identify options, evaluate alternatives and recommend a selected alternative(s) for processing HLW Tank 48H contents to a waste form capable of being processed or stored by existing or planned facilities.

During Phase 1 multiple approaches were used to identify alternative processes to meet the production and safety requirements for tank disposition. Formal brainstorming sessions with a range of stakeholders were supplemented by historical reviews and literature surveys. In addition, a Briefing Package for soliciting site wide experience was distributed to SRS Operations, Engineering and DOE.

The resulting list of 40 alternatives was screened against a set of minimum screening criteria, which included engineering maturity, safety, and permitting. Alternatives were either accepted as written, modified by combination or addition, or dropped. Ranking was performed within four decomposition categories to focus on the alternatives with the highest potential for success. The result of the exercise was an "Initial List" of fifteen alternatives selected as written or in part for further evaluation.

The focus of the Team's work in Phase 2 was on the technical investigation of the initial alternatives, the identification of technical risk and the application of selection criteria for complexity, science maturity, interfaces and process rate to establish a short list for further evaluation.

Table I. Tank 48 Phase 2 Alternatives List

Alternative #	Alternative Description	How?
3*	Feed KTPB Slurry to DWPF Salt Cell for Catalytic Decomposition	Thermal + Catalytic + Acidic
6	Catalytic Decomposition of TPB in a New or Existing Facility	Thermal + Catalytic + Acidic
5	Catalytic Decomposition of TPB Directly in Tank 48	Catalytic
7	Catalytic Decomposition of TPB Directly in Tank by Lowering pH (Acid Addition)	Acidic
11	Thermal Decomposition of TPB	Thermal
37	Hybrid – Microwave Destruction of Organics	Thermal
39	Steam Reforming/Fluidized bed Destruction of Organics	Thermal
38	Volume-Reduce by Filtration, Sending Filtrate to Tk 50, Catalytic Decomposition of Residual In-Tank	Catalytic
33	Catalytically Decompose TPB Using Tank 49 as a Reaction Vessel	Catalytic
35	Hybrid – Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate	Oxidation
36	Hybrid – Tank In Tank	
8	Oxidation of TPB Using UV Catalyzed TiO_2	Catalyzed Oxidation
17	Distribute Among Other Tank	Data Study
18	Direct Grout	Data Study
9	Oxidation of TPB Using Water Soluble Mild Oxidant	Oxidation
10	Oxidation of TPB Using Permanganate	Oxidation
23	In-Tank (or a coupled tank) Bioremediation	Bioremediation/ Contract
26	Hybrid – Metathesize with Cold Cesium	

The team came up with two broad recommendations. For processing options in new facilities, Acid Hydrolysis and Steam Reforming were the first and second choices. If Tank 48H could be used as a processing tank, permanganate and catalytic destruction also rated high. Later review teams added Fenton Chemistry and Wet Air Oxidation to the list of processing options.

Hydrolysis Options

The most technically mature of the processes was the copper catalyzed acid hydrolysis process planned for use in DWPF (11,12,13). However, because of the small volume of waste requiring processing (approximately 20,000 liters if concentrated to 10 wt% insoluble solids, just 3 DWPF batches), it was decided not to use the existing DWPF Salt Processing Cell for processing the precipitate in Tank 48H. Hence, any use of this process would require the construction of new, smaller facility to replace ITP and the DWPF Salt Cell. The resulting facility would also have to decompose the benzene stream as SRS's incineration facility was shut down soon after ITP. As a result, the acid hydrolysis process was never actively pursued once the process was chosen for the new Salt Waste Processing Facility.

Hydrolysis of the tetraphenylborate anion proceeds through a series of sequential reactions that ultimately must convert phenylboronic acid to boric acid and benzene (or other organic byproducts) to achieve complete conversion. The overall reaction is summarized below. There

are dozens of postulated reactions (14) for producing the organic byproducts typical of acid hydrolysis reactions, but these are omitted for brevity.

$B(C_6H_5)_4^- + 4H_2O \rightarrow 4C_6H_6 + B(OH)_4^-$ (Eq. 1)

Oxidation Options

A number of oxidation options, including permanganate oxidation, Fenton Chemistry, steam reforming and wet air oxidation were considered as each would lead to the complete decomposition of TPB and benzene, one disadvantage of hydrolysis options. Steam reforming was highly rated because of its maturity in processing radioactive waste. This is the preferred processing option at SRS and continues to be pursued. Wet air oxidation is being pursued as a potential backup option at SRS. These options will not be discussed in this paper as they will be discussed by other authors.

Fenton's Reagent (15) utilizes peroxide catalyzed by iron at pH 3-5 to generate hydroxyl free radicals, a very strong oxidizing agent. It should be noted that the optimum pH region for the Fenton reaction and Acid Hydrolysis are both pH 3.5. In addition, the normal catalyst for the Fenton reaction is iron but other transition metals, particularly copper are also effective. The hope was that the Fenton Reaction would be significantly faster than the hydrolysis reaction or that the Fenton Reaction would decompose the benzene prior to release to the offgas. However, the high benzene production in Fenton Experiments indicated that a significant reaction rate was due to the hydrolysis, not solely due to the Fenton Reaction.

The development of a caustic oxidizing process has the potential as an in-tank processing option, a potentially cheaper alternative. An in-tank process does not have to be fast as it may take 1-3 years to complete the processing in a new processing facility. Therefore, the development of the in-tank process should lead to complete decomposition in less than one year, minimizing the production of benzene.

In the presence of a transition metal catalyst, such as iron, hydrogen peroxide degrades to form the even more powerful hydroxyl radical via the reaction:

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\bullet$ (Eq. 2)

hydroxyl radical

Under acid conditions, the hydroxyl radical has a standard reduction potential of 2.7V and is the second most powerful oxidizing species known, after elemental fluorine. It reacts readily with organics through two main pathways:

The overall oxidation reaction may be written as:

$(C_6H_5)_4B^- + 60H_2O_2 \rightarrow 24CO_2 + 70H_2O + BO_2^-$ (Eq. 3)

319g 2040g 1056g 1260g 43g

so that complete destruction of 1g of TPB at 1:1 stoichiometry requires 6.39g of pure hydrogen peroxide.

The competing 'wasteful' reactions make it impossible to achieve a stoichiometric reaction in practise.

RESULTS

The approach for development of the four processing alternatives varied widely. For example, two decades, involving thousands of experiments, from small laboratory experiments to full scale processing was completed in the development of the acid hydrolysis process. In contrast, the caustic oxidation process involved less than ten experiments, mainly scoping in nature. Thus the maturity of these processing alternatives varied dramatically.

Significant results for these four processing alternatives are discussed in this section. For acid hydrolysis, the discussion is a summary of literally thousands of tests. For the other three alternatives, the results of significant experiments will be summarized. Additional reports contain further details than can be summarized in this report.

Acid Hydrolysis

Hydrolysis of the tetraphenylborate anion to boric acid and organic products (primarily benzene) proceeds through a sequential series reaction network that ultimately must convert phenylboric acid to boric acid, benzene, and other organic byproducts to achieve complete hydrolysis. Hydrolysis of phenylboric acid requires removal of the last phenyl group from the boron atom that was in tetrahedral coordination to four phenyl groups in the tetraphenylborate molecule. This is generally acknowledged to be the slowest step in the reaction network representing the complete hydrolysis of tetraphenylborate, requiring temperatures of about 150 'C in the absence of any catalyst (15). Although many metals exhibit some catalytic effects on the rate of phenylboric acid hydrolysis, copper is by far the most active identified catalyst (16) and is used to achieve acceptable reaction rates and conversions of phenylboric acid at ambient pressures and temperatures of about 90-101 °C (17).

Acid hydrolysis was chosen as the baseline process for the destruction of the TPB present in Tank 48H (18,19). The TPB feed to DWPF was approximately 10 wt % insoluble solids (8.45 wt% TPB) and 0.01 M nitrite ion. The acid hydrolysis process evolved from the original plan to process the feed at 0.20 M nitrite (original flowsheet, 20) to a hydroxylamine nitrate addition to destroy nitrite prior to hydrolysis (HAN flowsheet, 21) to the final flowsheet that added a late wash facility to wash the nitrite down to 0.01 M (late wash flowsheet, 19). Only the results from the late wash flowsheet will be discussed.

Hundreds of late wash flowsheet experiments were completed to develop and demonstrate the process. This included fourteen one-fifth scale experiments (22) (~1000-gallon batch size) in the Precipitate Hydrolysis Experimental Facility (PHEF) and nineteen full-scale demonstrations (~5000-gallon batch size) in DWPF with simulant (23). In addition, two experiments with actual waste were completed to demonstrate the viability of the flowsheet (24).

The liquid products of acid hydrolysis were a very low radioactivity organic stream (primarily benzene with other decomposition byproducts) and an aqueous stream containing almost all the radioactivity. The tetraphenylborate was completely destroyed. The aqueous product was purified using steam stripping/extraction of the organic decomposition byproducts. The aqueous stream was fed to the DWPF Chemical Processing Cell for inclusion in the DWPF glass canisters. The organic stream would have to be incinerated or otherwise processed by an offsite vendor.

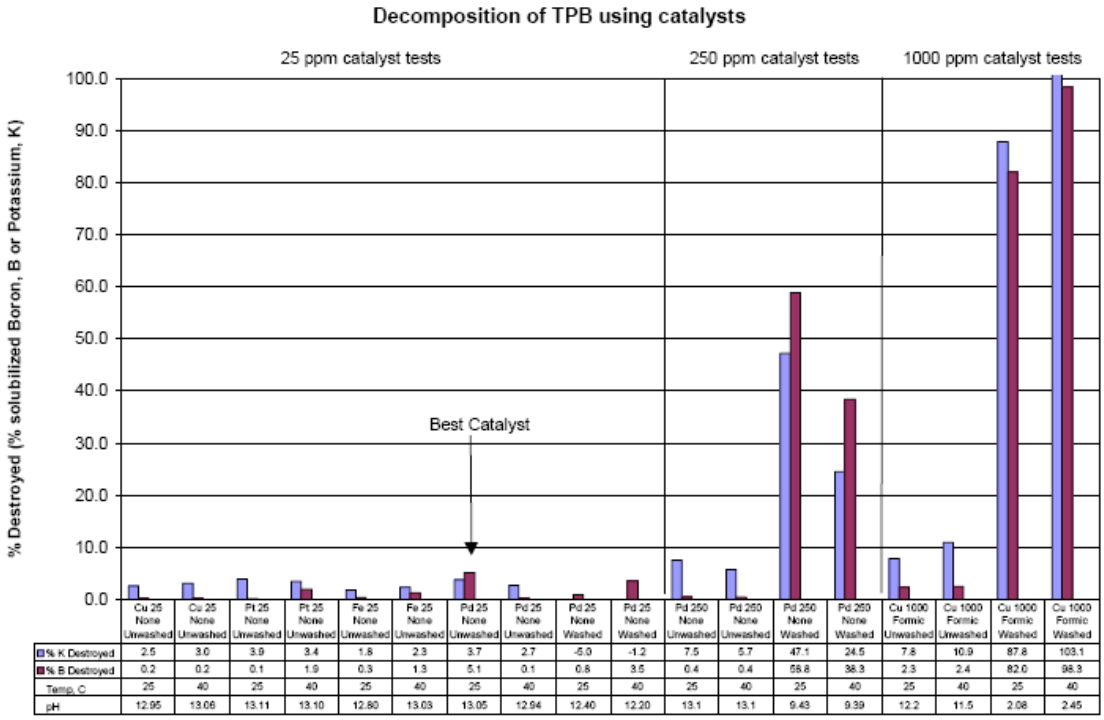
Approximately 99% of the tetraphenylborate decomposed to benzene. To maximize reaction rates and minimize byproduct generation, the hydrolysis occurred at 90 °C and the steam stripping occurred at approximately 100 °C. The generation of large quantities of benzene led to

processing under inert conditions (dilution of the offgas with nitrogen gas to exclude oxygen) to ensure a flammable mixture would not form.

Caustic Hydrolysis

Hydrolysis and catalyzed destruction of the organic material within Tank 48H were considered as processing alternatives for an in-tank process. Previous testing focused on thermal and copper catalyzed destruction of the tetraphenylborate as a potential treatment. (25,26) Testing employed simulants in both static bottle tests and dynamic laboratory-scale instrumented demonstrations. While some initial tests in 2003 (27) showed almost complete destruction, later stimulant tests in 2004 failed to duplicate these results. (28) A few static bottle tests used simulated waste. The lack of sufficient reactivity in these tests resulted in a SRNL Peer Review of the program. (29) The conclusion of that Peer Review resulted in the use of palladium (Pd) as the catalyst. The Pd catalysis of tetraphenylborate slurry is a known method to produce extensive TPB decomposition. (30)

Although acid hydrolysis is kinetically favored over caustic hydrolysis, the acidic conditions are much too corrosive to be completed in a carbon steel waste tank. However, if the appropriate processing conditions and catalyst could be found to allow in-tank hydrolysis to be feasible, it would save the cost of a new shielded facility. Testing with simulants identified conditions that led to decomposition of TPB via the addition of catalyst, lowering the pH, and increasing the liquid temperature. As each of these actions can be accomplished in-tank, these results suggested that an in-tank caustic hydrolysis process could be developed. The successful scoping tests were completed at a pH of 9.5, a temperature of 40°C, and a palladium catalyst concentration of 250 mg/kg Pd. (27) Fig. 4. is a graph comparing various tests designed to find a suitable catalyst for the decomposition of TPB.



	Cu 25 None Unwashed	Cu 25 None Unwashed	Pt 25 None Unwashed	Pt 25 None Unwashed	Fe 25 None Unwashed	Fe 25 None Unwashed	Pd 25 None Unwashed	Pd 25 None Unwashed	Pd 25 None Washed	Pd 25 None Washed	Pd 250 None Unwashed	Pd 250 None Unwashed	Pd 250 None Washed	Pd 250 None Washed	Cu 1000 Formic Unwashed	Cu 1000 Formic Unwashed	Cu 1000 Formic Washed	Cu 1000 Formic Washed
% K Destroyed	2.5	3.0	3.9	3.4	1.8	2.3	3.7	2.7	-5.0	-1.2	7.5	5.7	47.1	24.5	7.8	10.9	87.8	103.1
% B Destroyed	0.2	0.2	0.1	1.9	0.3	1.3	5.1	0.1	0.8	3.5	0.4	0.4	58.8	38.3	2.3	2.4	82.0	98.3
Temp, C	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	40	25	40
pH	12.95	13.06	13.11	13.10	12.80	13.03	13.05	12.94	12.40	12.20	13.1	13.1	9.43	9.39	12.2	11.5	2.08	2.45

An eight-step plan for destroying the tetraphenylborate in the waste tank was developed and tested using a Tank 48 simulant. The eight processing steps include increasing the liquid temperature to 35 °C, then 45 °C (later revised to allow 55 °C), lowering the solution pH to 13, 12, and 11, adding copper catalyst to reach 6 and then 24 mg/L, and metering in hydrogen peroxide (H2O2) to completely destroy the tetraphenylborate and other benzene producing decomposition products in an effort to leave <370 grams of KTPB in Tank 48H. This would allow the tank to be returned to service and make the Tank 48H solution compatible with the rest of the High Level Waste system. An objective of the testing was to determine conditions where TPB decomposition rates were between 4 and 7 mg/L/h benzene (98.1 – 172 mg/L/day TPB decomposition) The decomposition rates proved too slow to be viable in Tank 48H.(28)

SRNL researchers ran fifteen experiments with actual Tank 48 waste to determine the feasibility of a caustic hydrolysis process for decomposition of TPB In-Tank. Only experiments 1-A, and 1-B will be discussed as these led to the most significant KTPB decomposition. Table II lists the experimental matrix.

Table II. Test Conditions for Caustic Hydrolysis Tests 1-A and 1-B, Experiments at 75 °C

Test ID	pH	Time = 0 Pd (mg/L)	Starting TPB (mg/L)	Tank 48H Slurry (mL)	DDI Water (mL)	40 wt % $NaNO_2$ Solution (mL)
1-A	11	26	8210	65.4	16.1	57.7
1-B	11	26	8210	65.2	16.1	57.6

The additions of water and sodium nitrite mimic the tank conditions required for corrosion control. (31) The high temperatures and elevated nitrate concentrations, from the nitric acid addition, requires a large concentration of nitrite anion to maintain the tank within the requirements of the corrosion control program.

After the pre-acid measurements, each experiment was adjusted to its starting pH value. The pH adjustments occurred over approximately three days. The technicians measured a final pH using a pH probe before proceeding to the next step of the experiments.

After the pH adjustment, each bottle was heated to 75 ºC. When the bottles reached reaction temperatures (normally within 1-2 hours), 1 mL of Pd solution was added to those experiments that required it (Experiments 1-A, 1-B).

The experiments monitored the decomposition of the organic (i.e., KTPB and CsTPB) at elevated temperature for each experiment. Personnel collected samples for chemical analyses. Chemical analyses included determination of ^{137}Cs concentration – as a measure of decomposition of the CsTPB – using the gamma counter available within the Cells. Selected samples also received potassium, boron, gammascan, and organic analysis by the SRNL/Analytical Development Section (ADS) outside the Cells using Inductively Coupled Plasma – Emissions Spectroscopy (ICP-ES), Atomic Absorption (AA) and High Performance Liquid Chromatography (HPLC).

Four sets of analyses were used to determine the destruction of the TPB. If the TPB is decomposing, the soluble gamma (i.e., cesium-137), potassium and boron concentrations should all increase and the total TPB concentration should decrease. As it is hard to get a representative sample of the slurry, filtered samples (0.45 µm filter) were analyzed for gamma using radioactive

counting methods, potassium by AA, and boron by ICP-ES. TPB was measured by analyzing slurry samples by HPLC.

For the 15 experiments, technicians collected a number of filtrate samples for in-cell gamma counting. The raw gamma-scan results are converted into "% TPB destruction" terms. The % TPB destruction is determined by the following equation:

$$\% \text{ TPB Destruction} = \frac{[Cs]_{s0} - [Cs]_{ft}}{[Cs]_{s0} - [Cs]_{f0}} \times 100\% \qquad \text{(Eq. 4)}$$

where $[Cs]_{ft}$ is the ^{137}Cs value in the filtrate at the sample time t, $[Cs]_{f0}$" is the calculated ^{137}Cs concentration in the filtrate at the start of the test, $[Cs]_{s0}$" is the calculated ^{137}Cs concentration in the slurry at the start of the test.

Only one experiment maintained the desired level of reactivity. Most experiments exhibited a reaction rate far lower than required. Within four hours of the time=0, Experiments 1-A and 1-B showed a color change (darkening) that may indicate a chemical reaction. Within 24 hours, these two solutions darkened considerably (Fig. 5.).

Fig. 5. Photograph of Actual Waste Early Into the Caustic Hydrolysis Tests

* The picture was taken 7-20-04, 1 day into Experiments 1-A, 1-B, 2-A, 3-A, and 4-A. Note the darker appearance of Experiments 1-A and 1-B.

Aside from the visual differences, analytical results show an immediate in-growth of soluble ^{137}Cs into the solutions (Table 3). In-growth of soluble 137Cs indicates decomposition of CsTPB (Figure 4). For the purposes of determining the extent of TPB decomposition, the 137Cs activity in solution was converted into a "percent completion" relative to complete destruction of TPB. In Experiments 1-A and 1-B, the reactions reached ~30% completion by 48 hours, and stopped after that point for the remainder of the sampling. The agreement between Experiments 1-A and 1-B is good; typically 5% units or less in variation.

The potassium data for Experiments 1-A and 1-B (Table III) agree well with the gamma scan data, differing by an average of ~3% points for those times that had both a gamma scan and potassium measurement. [WSRC-TR-2004-00505, REV. 0]

Table III. Cesium, Potassium and Boron Results for 1-A and 1-B

Time (hours)	Extent of Reaction (%)					
	Experiment 1-A			Experiment 1-B		
	Cs	K	B	Cs	K	B
0	5.79	5.09	-0.814	7.47	19.6	59.4
3	17.1	12.8	-1.24	16.8	14.1	4.41
6	20.5	21.1	2.62	22.2	18.4	9.56
24	28.3	21.8	6.05	29.2	24.1	15.6
48	27.0	16.2	-6.82	29.7	23.9	20.7
94	25.6	22.6	NA	29.0	NA	NA
168	24.3	22.3	NA	25.4	NA	NA
214	25.8	22.5	12.9	27.1	24.6	19.4
260	24.8	22.1	NA	27.1	NA	NA
335	25.1	27.9	NA	27.5	NA	NA

NA = Not Analyzed

From the TPB destruction values in Table III, the rates of benzene generation (and TPB destruction) can be calculated (Table IV). The rates are calculated as cumulative rates, from time = zero to the time of each data point.

Table IV. Rate of Benzene Production and TPB Destruction for Experiments 1-A and 1-B from Gamma Scan Data

Time (hours)	Cumulative Rate of Reaction			
	Experiment 1-A		Experiment 1-B	
	Rate of Benzene Production, mg/(L-hour)	Rate of TPB Destruction, mg/(L-hour)	Rate of Benzene Production, mg/(L-hour)	Rate of TPB Destruction, mg/(L-hour)
3	240	245	193	197
6	171	174	174	177
24	65.8	67.1	63.6	64.9
48	30.5	31.1	31.9	32.5
94	14.4	14.7	15.7	16.0
168	7.61	7.76	7.38	7.53
214	6.43	6.56	6.30	6.43
260	5.03	5.13	5.20	5.30
335	3.97	4.05	4.12	4.20
576	1.80	1.84	1.78	1.82
744	1.37	1.40	1.48	1.51
1104	1.23	1.25	Experiment Terminated at 744 hours	
1224	0.903	0.921		

Both Experiments 1-A and 1-B showed an initial rapid reaction, peaking at a rate of 217 ± 24 mg/(L-hour) benzene generation (i.e., the average of Experiments 1-A and 1-B at 3 hours). However, while the reaction was rapid, it also stopped between 24 to 48 hours. From that point onward, a decline in rate is noted because the reaction has slowed or halted. Because of the low extent of reaction (<30%), the caustic hydrolysis reaction path was abandoned.

Acidic Peroxide Oxidation

The work for development of an out of tank oxidation process was led by AEA Technology (32) with support from Paul Taylor of the Oak Ridge National Laboratory (33). AEA Technology worked for approximately 15 years on the development, demonstration and application of a low temperature, low pressure technology for the destruction of organic waste. The process uses catalyzed hydrogen peroxide to oxidize organic material, with the main products being carbon dioxide, water and inorganic salts. The oxidative powers of the system have been known for over 100 years (34), with this type of chemical reaction now commonly known as a Fenton type reaction. AEA Technology has taken the basic chemistry and applied it to the processing of radioactive waste at engineering scale. AEA Technology's application of the technology is known as the ModulOx™ process.

AEA Technology embarked on a laboratory scale experimental program, using simulant materials, the primary purpose being to demonstrate that the process could be successfully applied to the Tank 48 waste. In addition to demonstrating that the process is capable of

destroying TPB effectively, the secondary purpose of the program was to gather data on the specific application of the process to Tank 48 waste and to begin definition of a reaction scheme.

AEA Technology developed an acidic Fenton Process using a Tank 48 simulant at laboratory scale. The majority of experiments used batches of approximately 100ml of Tank 48 simulant. The main results from the trials are summarized in Table V. AEA Trials 1-3 were scoping trials and data are therefore not presented in the table.

Table V. Summary of AEA Trials on T48 Simulant

Trial	Starting Simulant (g)	Starting TOC[1] (g)	Catalyst (ppm)[2] Fe	Catalyst (ppm)[2] Cu	1st pH Adjustment	2nd pH Control	50wt% H_2O_2 (g)	Stoichiometric Ratio[3]	TOC (ppm)
AEA4	113.6	18,700	200	200	7.5	3.5	62.4	2.1	570
AEA5	110.1	18,600	200	200	7.5	3.5	50.7	1.8	640
AEA9	110.2	18,700	200	0	7.5	3.5	77.0	2.7	840
AEA10	110.0	18,600	200	0	7.5	3.5	74.6	2.6	860
AEA 11	111.0	18,800	100	0	7.5	3.5	67.6	2.3	800
AEA 12	107.3	18,600	0	200	7.5	3.5	60.3	2.2	320
AEA 13	107.9	18,600	0	100	7.5	3.5	73.3	2.6	450
AEA 14	104.0	18,700	200	200	7.5	3.5	79.8	2.9	220
AEA 15	101.3	18,700	200	200	7.5	3.5	69.0	2.6	560
AEA 16	101.8	18,700	0	0	7.5	3.5	68.4	2.6	980
AEA 18	101.1	18,700	0	400	7.5	3.5	72.8	2.8	880
AEA 21	100.5	18,700	0	200	7.5	3.5	70.1	2.7	860
AEA 22	100.3	18,600	0	200	7.5	3.5	67.7	2.6	740
AEA 23	104.5	18,700	0	200	7.5	3.5	67.3	2.5	1,540

1. Starting TOC is calculated assuming 23g/l TPB, i.e. 21g/l TOC.
2. Concentration of catalyst in an assumed starting volume of 100ml. The concentration declines during neutralization and subsequent reaction.
3. Based on a stoichiometric reaction of 0.261g of 50-wt% H_2O_2 per 1g of simulant. No allowance is made for competing oxidation reactions, e.g. oxidation of nitrite to nitrate.

AEA recommended processing at the following reaction parameters:

- 200 ppm copper only catalyst,
- Initial adjustment of pH to 7.5,
- Operation at boiling point,
- Later control of pH to around 3.5,
- 2.5 X stoichiometric addition of 50-wt% hydrogen peroxide.

At the completion of AEA's process development, five additional tests with Tank 48 simulant were performed at ORNL for two reasons, namely to perform testing at a larger scale and to measure the composition of the offgas produced. The amount of acid, base, and peroxide used for each ORNL test is summarized in Table VI. The 350 mL of 50-wt% peroxide added is 2.5 times the stoichiometric amount needed to convert all of the TPB in 500 mL of simulant to carbon dioxide and water. Sodium hydroxide was not needed for pH control.

Table VI. Summary of chemical additions for each ORNL test and destruction efficiency

Test #	Catalyst	5 *M* HNO_3 (mL)	1 *M* NaOH (mL)	50% H_2O_2 (mL)	% TOC Removed
ORNL1	200 mg/L of copper and 200 mg/L of iron	260	0	350	>99.9
ORNL2		252	0	350	99.7
ORNL3		261	0	350	98.4
ORNL4	200 mg/L of copper	258	0	350	99.5
ORNL5		257	0	350	99.4

The feed slurries, intermediate samples, and the final treated slurries were analyzed for TOC. The percentage of TOC removal for the treated samples from each test is calculated using the measured TOC concentrations in the feed simulants. Table VI summarizes the TPB destruction efficiency.

The final treated slurries from each test were also analyzed for semi-volatiles. Several identifiable compounds were present at low concentrations (0.1–1.0 mg/L), including phenol, biphenyl, *N*-nitrosodiphenylamine, 2-nitrophenol, 4-hydroxy-4-methyl-2-pentanone, and *N*,*N*-diphenylbenzenamine. Two of the samples were analyzed for benzene, but the concentration was less than the detection limit of 0.001 mg/L. A large amount of benzene was formed during the treatment of the simulant samples, but it apparently all evaporated from the boiling slurry. The treated slurries were also analyzed for TPB and its breakdown products using HPLC. These compounds were not detected in any of the samples. The detection limits are 30 mg/L for TPB, 3 mg/L for triphenyl borane, 5 mg/L for phenylboronic acid, and 10 mg/L for phenol.

One composite sample of all of the off-gas and a sample of the final gas sample were analyzed for organics by GC-MS. For test ORNL2 (higher pH), the composite off-gas sample contained 11,000 ppm_v of benzene and the last off-gas sample contained 1400 ppmv of benzene. No other organics were detected in the samples. For test ORNL3 (lower pH), the benzene results were much lower, 1668 ppm_v in the composite sample and 341 ppm_v in the final sample. Trace amounts (<20 ppm) of acetone, acetaldehyde, phenol, and a nitrosubstituted alkane were also detected in both samples.

A carbon balance for tests ORNL 4 and 5 was calculated from the analytical results of the treated slurry, off-gas, and condenser residue for these tests. The results are shown in Table VII. The TOC results were used to calculate the amount of carbon in the treated slurry and in the residue from the condenser and off-gas line. The GC results for CO_2, CO, and benzene were used to calculate the carbon in the off-gas. The carbon in the starting simulant was calculated from the amount of TPB added, rather than using the TOC results, which were lower than expected, possibly due to hydrolysis of the TPB during drying of the samples.

Table VII. Carbon balance for ORNL Tank 48H treatment tests

Description of Source	Moles of Carbon	
	Test ORNL4	Test ORNL5
Benzene in off-gas	0.365	0.193
CO_2 in off-gas	0.302	0.168
CO in off-gas	0.005	0.002
TOC in slurry	0.002	0.002
Off-gas deposits	0.011	0.004
Total	0.685	0.369
Starting simulant	0.873	0.873
Recovery (%)	78.5	42.3

If the benzene results from the GC-MS analysis are used in place of the GC results, the amount of carbon in the off-gas due to benzene changes to 0.042 mol for test ORNL4 and 0.303 mol for test ORNL5, and the carbon recovery changes to 41.6 and 55.2%, respectively. The increased benzene concentration measured by the GC-MS in the first two composite off-gas samples for test 5, rather than the very high concentration measured in the headspace sample, is the main contributor to the increased amount of carbon in the off-gas, since the headspace sample represents a low gas volume.

The acidic peroxide process led to quick and complete destruction of the sodium tetraphenylborate. The process also produced a large quantity of benzene, not just the carbon dioxide that was expected. This led to a concern that safety operating a Fenton reactor would be difficult due to the fact that both oxygen and benzene are being produced during processing. The development of a process that would produce very little benzene would be needed to make this a viable process. An alternative catalyst system would be needed prior to pursuing acidic peroxide oxidation of TPB.

Caustic Peroxide Oxidation

In Pd-catalyzed tetraphenylborate decomposition, the primary products of the reaction include benzene, phenol and borate salts. In Tank 48H, the benzene would be released to the tank vapor space and removed from the tank by the existing nitrogen purge ventilation system. The phenol and borate salts remain within the tank liquid along with the monosodium titanate and sludge solids. Once analysis shows the material meets the end state requirement for Tank Farm service, personnel may transfer the resulting liquid to any Tank Farm waste tank or concentrate the waste in the HLW evaporator system.

Approximately sixty experiments were completed in 2003 to identify the appropriate catalyst for the development of a caustic peroxide oxidation process. (35) A number of transition and noble metals, along with several catalyst combinations, were tested. In addition, a promising new class of catalysts, the TAML® (Tetra-Amido-Macrocyclic-Ligand) family of catalysts developed by Terry Collins of Carnegie Mellon University was also tested. (35) Although many of these experiments were successful in destroying most of the TPB, the cost of the TAML® catalysts and concern over the availability of the sufficient catalyst led to abandoning the use of the TAML®

catalyst in further studies. Based on the results of this testing, copper was chosen as the catalyst in future testing.

Three experiments were completed in FY04 using copper as the catalyst for peroxide oxidation (36). The first experiment used a depleted simulant, designed to predict the composition in Tank 48H after copper catalyzed hydrolysis destroyed 85% of the TPB. (28) The other two experiments used the Tank 48H simulant, using copper catalyst to destroy the TPB present. (31) The experiment at pH 11 led to complete destruction of TPB.

The primary objective of the testing was to measure the extent of TPB decomposition. In addition, the liquid and vapor were analyzed to understand and quantify the decomposition products present during the reaction. At the completion of the testing, measurements provided a gross measure of the general corrosion rate to the carbon steel reaction vessel.

For the pH 11 experiment, the final slurry TPB concentration was less than 10 mg/L, the detection limit for this sample. This indicates that >99.8% of the TPB was destroyed during the testing. For the pH 14 experiment, the final slurry TPB concentration was 1,310 mg/L compared to a starting concentration of 1,690 mg/L. This equates to 22% TPB decomposition for the pH 14 experiment.

For the pH 11 experiment, the K concentration in the filtrate exceeded the K concentration in the slurry for a calculated 100% TPB decomposition. The calculated TPB decomposition was 95% based on the B analyses. These analyses confirm the HPLC decomposition calculation in the pH 11 experiment. Note 48.0% of the K and 32.7% of the B was soluble in the slurry before testing began. The increase in soluble K and B was used to calculate the % TPB decomposition. Table VIII summarizes the data from the pH 11 experiment.

Table VIII – TPB Decomposition Based on Results of pH 11 Filtrate and Slurry Samples Pulled at Completion of Caustic Peroxide Testing

Sample ID Analysis	Filtrate	Digested Slurry	Predicted Slurry Composition	% TPB Decomposition
ICP-ES B, mg/L	345	363	403	95%
ICP-ES K, mg/L	1470	1320	1550	100%
AA K, mg/L	1550	NA	1550	100%

Table IX shows the results for the pH 14 experiment. For the pH 14 experiment, 4-10% decomposition was noted based on the filtrate and slurry values. The percentage decomposition is calculated by comparing the filtrate concentration to the predicted slurry composition.

Table IX – TPB Decomposition Based on Results of pH 14 Filtrate and Slurry Samples Pulled at Completion of Caustic Peroxide Testing

Sample ID Analysis	Filtrate	Corrected Starting Filtrate Composition	Predicted Slurry Composition	% TPB Decomposition
ICP-ES B, mg/L	50.9	6.54	389	10.3%
ICP-ES K, mg/L	376	263	1687	7.9%
AA K, mg/L	321	NA	1687	4.1%

A single HPLC analysis of a sample pulled at the end of the experiment gives a snapshot of the TPB and TPB decomposition products present in that sample. For the pH 11 all thirteen typical TPB decomposition products in a slurry sample analyzed at the conclusion of testing (triphenylboron, 2PB, phenylboronic acid, phenol, nitrobenzene, nitrosobenzene, 4-phenylphenol, 2-phenylphenol, diphenylamine, biphenyl, o-terphenyl, m-terphenyl, and p-terphenyl) were less than the 10 mg/L detection limit. Besides TPB, the slurry also began the test with approximately 700 mg/L of phenol. Both tests destroyed phenol present in the feed or produced during testing.

The addition of 1.1064 g of $CuSO_4 \cdot 5H_2O$ (0.315 g Cu added to 674 mL of slurry) led to a 467 mg/L increase in the copper concentration on 10-8-2004. The copper addition correlates strongly with the destruction of TPB for the following reasons. First, no detectable TPB decomposition occurred before the addition of copper. The soluble K and B concentration increased after addition of copper, indicating that the TPB was being consumed. Second, the offgas oxygen concentration dropped from a steady value of 7 vol % to 6 vol % after the addition of the 467 mg/L copper. If no peroxide is added, the expected oxygen concentration is 5 vol %. (i.e., the concentration entering the vessel) If none of the peroxide is oxidizing the TPB, it will react with itself decomposing to oxygen and water (explaining the 7 vol % oxygen during the early part of the testing). Upon copper addition, the oxygen concentration dropped to ~6 vol %, indicative that approximately half of the peroxide was being consumed in oxidation reactions. Figure 6 summarizes the calculated TPB decomposition based on filtrate K analyses.

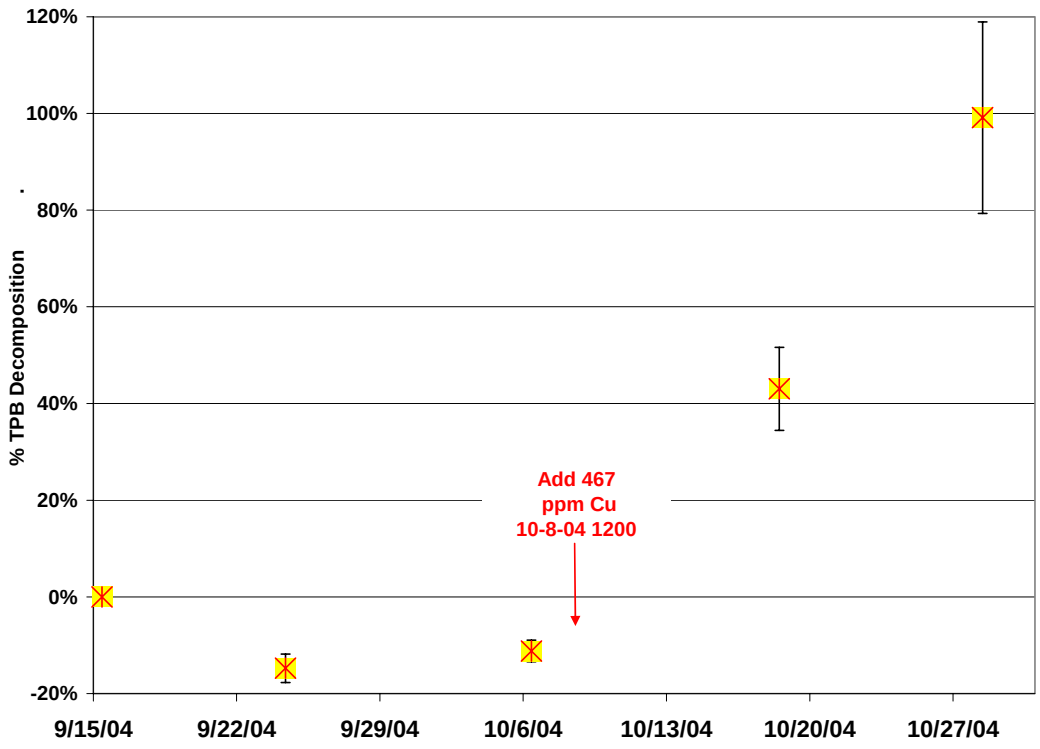


Fig. 6. Calculated % TPB Decomposition for pH 11 Caustic Peroxide Experiment

SUMMARY

Four processing alternatives were discussed and contrasted in this document. None of these alternatives is being pursued at SRS. The acidic processes could likely be successfully implemented in new, engineered processing facilities. The acidic Fenton process would take more development effort, including the demonstration of the process with actual waste and at the pilot scale. Because of the maturity of the acid hydrolysis processing, this process could be implemented with less development work. The in-tank caustic processes would take considerably more effort to develop and would only be recommended to minimize the cost of TPB processing. Any in-tank process is riskier since the processing is taking place in a very large tank that was not designed to process TPB and the processing itself could lead to excessive corrosion of the Tank itself. The advantages and disadvantages of all these processes are listed below:

1. The acidic hydrolysis process is the most mature and robust of the processes compared. Several issues remain with this process including whether the Tank 48H slurry should be filtered and washed prior to processing, and how to dispose of the benzene stream that is produced. However, this process is more mature and robust than any of the alternatives that have been studied to date, including steam reforming. This process requires minimal development compared to the rest of the alternatives.

2. The acidic Fenton process led to quick and complete TPB decomposition but produced significant benzene and oxygen, which would complicate processing to prevent flammability problems. To implement this in a new processing facility, processing conditions should be identified to minimize benzene generation and oxygen production. This likely would involve the use of an alternative catalyst as copper likely maximizes the rate of benzene generation.

3. The caustic hydrolysis process was abandoned due to incomplete TPB decomposition in experiments with actual waste. If this process would be reconsidered, a better catalyst or higher concentration of the Pd catalyst would be needed to ensure the complete decomposition of TPB. Development of the process with simulants, pilot-scale testing and actual waste testing would be needed prior implementation.

4. The caustic peroxide process led to complete TPB decomposition with simulants but has not been demonstrated with actual waste. If this process would be reconsidered, additional simulant testing would be needed to ensure the robustness of the process for complete decomposition of TPB. Demonstration in pilot-scale testing and actual waste testing would be needed prior to implementation.

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